

Shinbum article. In addition to Applicants' remarks in regard to this rejection in Applicant's prior response, please consider the following:

The date of the Asahi Shinbum article is November 28, 1986. As stated in Applicants' specification at page 6, lines 7-10:

The basis for our invention has been described by us in the following previously published article: J.G. Bednorz and K.A. Mueller, Zeitschrift for Physik B - Condensed Matter, 64, pp. 189-193, Sept. (1986).

The Examiner is using Asahi Shinbum as a reference under 35 USC § 102(a). Applicants respectfully disagree since to do so does not permit Applicants the one year period provided under 35 USC § 102(b) to file a U.S. application after their own publication which permitted Applicants to file the present application up to September 1987. The date of the Asahi Shinbum article is after the date of Applicants' publication.

In regard to the two-year grace period under a prior statute, the U.S. Supreme Court in *Andrews v. Hovey*, 123 US 267 (1887) states that:

"The evident purpose of the section was to fix a period of limitation which should be certain, and require only a calculation of time, and should not depend upon the uncertain question of whether the Applicant had consented to or allowed the sale or use. Its object was to require the inventor to see to it that he filed his application within two years from the completion of his invention, so as to cut off

all question of the defeat of his patent by a use or sale of it by others more than two years prior to his application, and thus leave open only the question of priority of invention. The evident intention of congress was to take away the right (which existed under the act of 1836) to obtain a patent after an invention had for a long period of time been in public use, without the consent or allowance of the inventor; it limited that period to two years, whether the inventor had or had not consented to or allowed the public use."

From this quote from *Andrews v. Hovey*, it is evident that the use or sale by others prior to filing a patent application by the inventor does not cut off the inventors right to obtain a patent so long as the inventor files the application within the statutory period which was 2 years at the time of the *Andrews v. Hovey* decision and is now 1 year under 35 USC 102(b).

The Patent Office Board of Appeals in *Ex parte Powell and Davies*, 37 USPQ 285 states in regard to the publication of Applicants foreign patent application before the filing of a U.S. application on October 5, 1936 on an invention described in the foreign patent application that:

The Examiner has also rejected the claims on the printed specification of Applicants' own British application which appears from this record to have been published on August 27, 1936. We know of no authority for such a rejection. Neither section 3886 nor section 4887 R.S. warrants the rejection. Obviously, the publication could not have a date

prior to Applicants' invention. There is no statute that requires an Applicant to make his invention in this country.

Therefore, Applicants of the present invention can rely on their publication in Zeitschrift for Physik as evidence of their invention.

The Patent Office Board of Appeals in Ex parte Powell and Davies, 37 USPQ 285, 286 further states:

The Commissioner indicates in Ex parte Grosselin that the Examiner should consider whether the German patent was derived from Applicant and was in effect nothing more than a printed publication of Grosselin's invention.

The Asahi Shinbun article states in the first paragraph:

A new ceramic with a very high T_c of 30K of the superconducting transition has been found. The possibility of high T_c - superconductivity has been reported by scientists in Switzerland this spring. The group of Prof. Shoji TANAKA, Dept. Appl. Phys. Faculty of Engineering at the University of Tokyo confirmed in November, that this is true.

The "scientists in Switzerland" are the inventors of the above-identified application. The Asahi Shinbun article only reports the work of Applicants and that it was reproduced by Prof. Tanaka. This article is a disclosure of Applicants' "own invention" and clearly

in the words of the Board in Ex parte Powell and Davics, "was derived from [Applicants] and [is] in effect nothing more than a printed publication of [Applicants'] own invention and cannot be used as a reference.

The Patent Office Board of Appeals in Ex parte Lemieux 148, 140 states that:

Finally, we believe that our holding is consistent with decisions in interference practice wherein, even though in the usual case a party may not establish a priority date of invention by reference to activity in a foreign country, yet in an originality case where a party is seeking to prove that the other party derived from him so that there is only a single original inventor, he may be permitted to prove derivation by reference to activity abroad. ... By analogy, in the present case appellant has demonstrated that he is the single original inventor, there being no adverse party.

Following this decision it is clear from the Asahi Shinbum article that Applicants are the "single original inventor" and that the Asahi Shinbum article is "derived" from Applicants and that Professor Tanaka's work reported in the Asahi Shinbum article is "derived" from Applicants.

Therefore, the Examiner is respectfully requested to withdraw the rejection of claims 24-26, 86-90 and 96-108 under 35 USC § 102(a) as anticipated by Asahi Shinbum and under 35 USC § 103 as obvious over Asahi Shinbum.

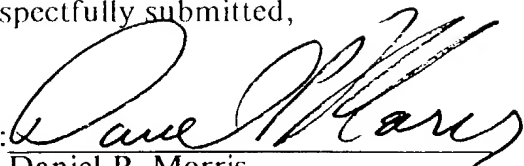
Attached are copies of the following decisions:

Ex parte Powell and Davies 37 USPQ 285

Ex parte Lemieux 115 USPQ 148

Respectfully submitted,

By:



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Patent Office Board of Appeals

Ex parte LEMIEUX

Patent issued Oct. 8, 1957

Opinion dated July 31, 1957

PATENTS

1. Interference—Reduction to practice—
In general (§ 41.751)

Patentability—Anticipation—In general (§ 51.201)

Patentability—Anticipation—Publications—In general (§ 51.2271)

Act of August 8, 1946 (35 U.S.C. 104) was enacted to overrule *Electric v. Shimadzu*, 307 U.S. 5, 41 USPQ 155, and preclude applicant or patentee from relying upon foreign activity to establish date of invention; it had no effect on *Ex parte Powell*, 37 USPQ 285; hence, inventor's foreign publication within year prior to filing United States application does not bar him from obtaining patent.

2. Affidavits—Anticipating references (§ 12.3)

Rule 131 does not apply where publication is publication of applicant's own invention; domestic inventors are not distinguished from foreign inventors; all that is required is that identity of application inventor and publication author be established.

3. Interference—Originality of invention—In general (§ 41.551)

Interference—Reduction to practice—
In general (§ 41.751)

Even though in usual case interference party may not establish priority date of invention by reference to activity in foreign country, in originality case, where party is seeking to prove that opponent derived from him so that there is only a single original inventor, he may be permitted to prove derivation by reference to activity abroad.

Particular patents—Ustilic Acids

2,809,205, Lemieux, Production of Ustilic Acids, claims 1 to 4 and 6 of application allowed.

Appeal from Division 63.

Application for patent of Raymond U. Lemieux, Serial No. 281,451, filed Apr. 9, 1952. From decision rejecting claims 1 to 4 and 6, applicant appeals. Reversed. *PIERCE, SCHEFFLER & PARKER*, Washington, D.C., and *ALEX E. MACRAE* for applicant.

Before *DUNCOMBE*, Examiner in Chief, and *MAGIL* and *BREWINK*, Acting Examiners in Chief.

MAGIL, Acting Examiner in Chief.

This is an appeal from the final rejection of claims 1 through 4 and 6. Claims 5 and 7, the remaining claims in the case, have been withdrawn from further consideration in accordance with Rule 142(b) and are not before us.

Since the issue involved in this case is purely legal in nature, there is no reason for reproducing an illustrative claim.

The reference relied upon is:

Lemieux, Canadian Journal of Chemistry, Vol. 29, (May 1951), pages 415-425.

We need not refer to the subject matter of the claims because, as previously indicated, the appeal involves only a legal point. The following facts are not in dispute:

1. The appellant is the author of the cited publication.

2. The subject matter of the appealed claims is adequately disclosed in the cited publication.

3. The cited article was published prior to appellant's filing date in this country, but not more than one year prior thereto.

4. Appellant does not rely upon any earlier filing date to antedate the publication, nor does he assert that he completed the invention in this country prior to the date of the publication.

The examiner holds that appellant is barred from obtaining a patent by the provision of 35 U.S.C. 102(a) and that he cannot avoid this bar because of the restriction of 35 U.S.C. 104 and the words "in this country" in Rule 131.

Appellant contends that he filed his application within the one year period specified in 35 U.S.C. 102(b) and that Rule 131 is inapplicable. Appellant relies upon the case of *Ex parte Powell* and *Davies*, 489 O.G. 231, 1938 C.D. 15, 37 USPQ 285; he also refers to the International Convention for the Protection of Industrial Property and to the effect of the examiner's rejection on Canadian inventors.

We have carefully considered the examiner's rejection and the appellant's arguments and have studied the pertinent cases on this subject. On its face, and disregarding subsequent statutory changes, the *Powell* and *Davies* case appears to be most apposite. The examiner recognizes that the cited decision is relevant, but holds that it is no longer controlling because of the Act of August 8, 1946, which resulted in the enactment of the statute presently corresponding to 35 U.S.C. 104.

[1] We have 35 U.S.C. 104 and by the case *Shimadzu et al.*, 307 U.S. 5, 41 O.G. 4, 41 in an infringement not precluded invention by abroad. We the *Shimadzu country*" in to present Rule the case of *Electric v. Shimadzu*, 307 U.S. 5, 41 F.2d 169, 52 the *Shimadzu* anomalous situation in another rule. In order the Act of August 8, 1946, as is evidenced by No. 1502, June 2nd Session, January 28, Session, the effect, to overturn the Act of August 8, 1946, include an appeal relying upon a date of invention case is referred to the Senate and the House of Representatives.

With the Act of August 8, 1946, it was said that the Act of August 8, 1946, to overrule the Act of August 8, 1946, it had no effect. *Davies* decision, *Powell* and *Davies*, 489 O.G. 231, 1938 C.D. 15, 37 USPQ 285, affected, we are trolling in the reversal of the note that there was cited by *In re Saurer*, 405, 529 O.G. 78, but the *C* applicable or failed to establish a person named also state that *Ex parte Granger*, C.D. 248, cite decision, as *Ex parte Granger*, C.D. 163, to

Aside from 104, there is no section is no case. Appellant's date of invention is argued that the publication of the examiner of invention

that he is the single original inventor, there being no adverse party.

In accordance with the foregoing reasoning, we conclude that the examiner's rejection cannot be sustained. We do not consider it necessary to discuss appellant's arguments concerning the International Convention for the Protection of Industrial Property or the effect of the examiner's rejection on Canadian inventors.

The decision of the examiner is reversed.

Patent Office Board of Appeals

Ex parte BERGMANN

Patent issued Oct. 8, 1957

Opinion dated Jan. 22, 1957

PATENTS

1. Patentability — Change — Material (§ 51.257)

Claims are allowed where applicant did not merely indulge in routine experimentation with material having properties which would be expected to produce results desired, but utilized to advantage a material whose properties appeared to be unfavorable.

Particular patents—Sound Recording 2,809,237, Bergmann, Magnetic Sound Recording Head, claims 1 and 3 to 7 of application allowed.

Appeal from Division 16.

Application for patent of Friedrich Bergmann, Serial No. 209,250, filed Feb. 3, 1951. From decision rejecting claims 1 and 3 to 7, applicant appeals. Reversed. MARZALL, JOHNSTON, COOK & ROOT, Chicago, Ill., for applicant.

Before TAYLOR and KREEK, Examiners in Chief, and NILSON, Acting Examiner in Chief.

KREEK, Examiner in Chief.

This is an appeal from the final rejection of claims 1 and 3 to 7 inclusive. No claims have been allowed.

Claim 1 is illustrative:

1. Magnetic sound recording head having a core consisting exclusively of magnetic ferrite.

The references relied on are:

Burns	2,536,260	Jan. 2, 1951
Buhrendorf	2,592,652	Apr. 15, 1952

As is apparent from the illustrative claim, the subject matter here on appeal relates to a recording head for a magnetic sound recorder in which the core consists exclusively of magnetic ferrite. Numerous advantages are claimed for this construction among which are reduction of wear on the core as a result of the magnetic record medium passing thereover, as compared to the wear of conventional iron cores under similar circumstances; and reduction in electrical losses especially at high frequencies.

Claims 1 and 3 to 7 were rejected as being unpatentable over Buhrendorf or Burns in view of the general knowledge of the art, the examiner's position being "The routine examination of any known substance for a particular use is expected where the known basic requirements of the use are compatible with some characteristics of the substance." It is his opinion "that the mere knowledge that 'ferrites' are magnetic is enough to warrant investigation by workers in magnetic recording. The knowledge of their high frequency losses and avowed utility in electro-acoustic devices practically demands investigation."

Appellant contends that the references relied on do not suggest making cores exclusively of ferrite, and that the known permeability, saturation and abrasive characteristics of ferrite would point away from its use in sound recording heads rather than suggest it. He asserts that recording heads heretofore used are made with cores of highly permeable material to secure proper operation, but that satisfactory operation is secured with ferrite cores even though the permeability thereof is considerably less than the magnetic materials previously used. He asserts that the smaller magnetic saturation of ferrite as compared with metallic magnetic material would tend to indicate its unsuitability in erasing heads where high magnetic saturation is required. He further asserts that the fact ferrite would not abrade the surface of the sound band was surprising since sintered ferrite behaves somewhat like sintered porcelain. This characteristic which would have been expected to be detrimental is alleged to provide a great advantage resulting in heads having a life at least ten times longer than that of metal heads heretofore used. Appellant has made of record a publication by Rolf Cruel in Technische Hausmittelungen des Nordwestdeutschen Rundfunks which compares magnetic heads made with ferrite with previously used laminated, high permeability iron alloy, which publication demonstrates important technical advantages possessed by ferrite over previously used magnetic materials. These are summarized as greater hard-

ness resulting in assistance to wear so used for much longer without adjustment high frequency and for erasing.

We have carefully in view of appellant various publication show the suitability material for recording of which we are of rejection cannot be

The patent to E magnetic recording netic materials such ing high permeability tions are made extr 0.001 of an inch th reduce eddy current value as is feasible ability to work with tions. Obviously I anticipatory value, b the problems confro this field as of the t Buhrendorf applicati

Burns shows a mag for magnetic recor utilize a central yoke either side of which iron pole pieces 11 an contact the surface o used in the recorder forms a part of the c tor, the frequency of a result of the variati flow through the fe noted, however, that pieces are necessary t netic tape from being frequency currents f wound in the ferrite n no suggestion in Bu core may be made of

[1] The examiner that low permeability factor as he states "s be undesirable perme undesired results." the teachings of the point away from the material having low as ferrite as the sol core for a sound recd withstanding this, t clearly shows that in permeability of ferrite netic properties are forms satisfactorily a magnetic recording nificantly, however, is made of ferrite have resistance to abrasion operate up to ten tim conventional metallic iron without adjustment. important factor in re

Patent Office Board of Appeals

Ex parte POWELL and DAVIES

Appl. No. 23985

Patent issued Apr. 5, 1938—Opinion dated Mar. 1, 1938

Patents—Patentability—Anticipation—Foreign patents; Affidavits—Anticipating references (Rule 75)—

Applicants' own British patent has not been sealed, so there is no reason for registry under Rule 29; the British application was published in Aug., 1936, but there is no authority for basing on it rejection of United States application filed less than two years after such publication; Rule 75 was intended to provide ex parte means by which applicant can overcome rejection based on publication not more than two years prior to his invention but does not apply to case where publication appears without question to be publication of applicant's own invention.

Patents—Electrodeposition of Silver—

2113517, Powell and Davies, Electrodeposition of Silver, claims 1, 2, 4 to 7, 10 and 11 of application allowed.

Patent No. 2113517 for electrodeposition of silver issued on application filed Oct. 5, 1936.

Appeal from Division 56.

HOWSON & HOWSON for applicants.

Before VAN ARSDALE, Assistant Commissioner, and REDROW and PORTER, Examiners in Chief.

PORTER, Examiner in Chief.—This is an appeal from the final rejection of claims 1, 2, 4 to 7, 10 and 11.

Claim 7 is illustrative.

7. A plating bath comprising a potassium argento-cyanide, an excess of free potassium cyanide, carbon disulphide and Turkey red oil.

The references relied upon are as follows:

Schlotter (British) 443,428, Feb. 27, 1936.

Powell et al (British) 450,979, Aug. 27, 1936.

Blum & Hogaboom, Principles of Electroplating (2nd Ed.) 1930, pages 350, 355 to 357.

It appears from Blum and Hogaboom that the silver plating solution of the claims is old except for the addition of alkali metal soaps or their equivalents. Blum et al describe an excess of free alkali metal cyanide but the British patent indicates that this excess should be very large and describes the use of Turkey red oil to which applicants refer at the bottom of page 3 of their specification. The British patent does not suggest the use of carbon bisulphide but rather suggests a substitute therefor. Blum et al does not suggest the use of soap. It is the combined use of carbon bisulphide and soap in the silver plating which applicants describe as their invention. The gist of the examiner's position with respect to the references referred

to appears to be that there is no invention in the combined use of the carbon bisulphide and soap in the silver plating bath. The trouble with this position is that it is not warranted by the record which does not show carbon bisulphide combined with a dispersing agent of the nature of the one employed by applicants.

The examiner has also rejected the claims on the printed specification of applicants' own British application which appears from this record to have been published on August 27, 1936. We know of no authority for such a rejection. Neither section 4886 nor section 4887 R. S. warrants the rejection. Obviously, the publication could not have a date prior to applicants' invention. There is no statute that requires an applicant to make his invention in this country.

It does not appear that the British patent has been sealed which sealing would be necessary in the case of a British patent in a rejection under Rule 29 and it appears from the decision of the Supervisory Examiner (Paper No. 7) that the examiner's real position is not that applicants are barred by the provisions of Rule 29 as appears from his statement, but that applicants have failed to overcome their own publication by affidavits filed under Rule 75.

Applicants filed a petition to the Commissioner asking that the examiner be instructed to withdraw the citation of their own British specification as a reference against the claims. This the Commissioner refused to do indicating that an adverse decision on the point by him might act to preclude a favorable decision by the Board of Appeals.

The examiner holds the affidavits insufficient as the nature of the contents of the notes referred to in the affidavit of Coussmaker does not appear and there is no such showing as to facts as is

necessary in affidavits filed under Rule 75. The affidavits have been reexamined but we find nothing therein except the mere inference that the subject matter in issue here was disclosed to Stones by Coussmaker.

The case of *Ex parte Grosselin* 1901 C. D. 248, is analyzed by applicants in such a way as to contend that this decision never was intended to apply to a case where the printed publication in question was one's own publication. There are, however, certain obiter statements made in the *Grosselin* decision which might be taken to indicate that the provisions of Rule 75 requiring the applicants to show completion of the invention in this country apply to a case wherein the applicant is required to overcome the filing date of his own publication. It is our opinion, however, that these obiter statements are not definite and any such construction of Rule 75 as contended for by the examiner is clearly refuted by the general tenor and intent of the decision. Rule 75 was intended to provide *Ex parte* means by which an applicant can overcome a rejection based on a publication of the invention not more than two years prior to his application. We do not agree with the examiner that this rule is intended to apply to a case where the publication

appears without question to be a publication of the applicant's own invention.

The Commissioner indicates in *Ex parte Grosselin* that the examiner should consider whether the German patent was derived from applicant and was in effect nothing more than a printed publication of *Grosselin's* invention. The decision further indicates that Rule 75 permits an applicant to make an *ex parte* showing of his rights (page 254) and that the whole proceeding is by analogy to the interference practice. On page 253 it is stated that, "Whenever this Office has satisfactory evidence that some other person is as against the applicant entitled to a patent, it is, under the general principles of the law which are well recognized, bound to reject the application."

Applicants' patent in Great Britain has not been sealed so that there is no reason for rejecting the claims under Rule 29 and it appears obvious that applicants made their invention prior to the date of their published specification.

It is our opinion that this record does not show prior invention of the subject matter of the claims by a party other than the applicants. They are, therefore, entitled to a patent.

The decision of the examiner is reversed.

Circuit Court of Appeals, Second Circuit
SHELDON et al. (complainants-appellees)

v.

MOREDALL REALTY CORPORATION (respondent-appellant)

No. 139

Decided Feb. 21, 1938

Copyrights—Pleading and practice in courts; Appeals to Circuit Courts of Appeals—Orders appealable—

Trial judge, recognizing non-existence of actual or threatened continued infringement, concluded in opinion that injunction should not issue, but apparently through inadvertence injunction was included in decree; appeal from that part of decree was properly taken; injunction is vacated and decree to that extent reversed; as jurisdiction to review interlocutory decree depends on 28 U. S. C. 227, general rule is that propriety of granting other relief forms no part of subject matter of appeal and is not before Circuit Court of Appeals, not being final decree, but rule is subject to one exception; where such appeal is rightly taken court may examine record thus made to determine whether bill is wholly lacking in equity and, if so, may dismiss; but where doubt exists as to equitable jurisdiction, that matter is left to appeal from final decree.

Copyrights—Pleading and practice in courts—

Copyright statute differs from patent and trade mark statutes, and injunction is not condition precedent for accounting and award of damages for copyright infringement; equitable jurisdiction having been invoked in good faith by suitable allegations in bill, jurisdiction may not fall with failure of proof on merits of exclusively equitable rights; nor can court be sure on appeal from interlocutory decree that equity does not have concurrent jurisdiction of accounting on general principles.

Patents—Jurisdiction of courts—For patent infringement—

In patent cases, only where injunction is rightly granted may there be accounting and award of damages in equity.

Possible High T_c Superconductivity in the Ba - La - Cu - O System

J.G. Bednorz and K.A. Müller

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Received April 17, 1986

Metallic, oxygen-deficient compounds in the Ba - La - Cu - O system, with the composition $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_{5(3-y)}$ have been prepared in polycrystalline form. Samples with $x=1$ and 0.75 , $y>0$, annealed below 900°C under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally an abrupt decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 30 K range. It is markedly reduced by high current densities. Thus, it results partially from the percolative nature, but possibly also from $2D$ superconducting fluctuations of double perovskite layers of one of the phases present.

1. Introduction

"At the extreme forefront of research in superconductivity is the empirical search for new materials" [1]. Transition-metal alloy compounds of $A15$ (Nb_3Sn) and $B1$ (NbN) structure have so far shown the highest superconducting transition temperatures. Among many $A15$ compounds, careful optimization of Nb-Ge thin films near the stoichiometric composition of Nb_3Ge by Gavalev et al. and Testardi et al. a decade ago allowed them to reach the highest $T_c = 23.3$ K reported until now [2, 3]. The heavy Fermion systems with low Fermi energy, newly discovered, are not expected to reach very high T_c 's [4].

Only a small number of oxides is known to exhibit superconductivity. High-temperature superconductivity in the Li-Ti-O system with onsets as high as 13.7 K was reported by Johnston et al. [5]. Their x-ray analysis revealed the presence of three different crystallographic phases, one of them, with a spinel structure, showing the high T_c [5]. Other oxides like perovskites exhibit superconductivity despite their small carrier concentrations, n . In Nb-doped SrTiO_3 , with $n = 2 \times 10^{20} \text{ cm}^{-3}$, the plasma edge is below the highest optical phonon, which is therefore unshielded

[6]. This large electron-phonon coupling allows a T_c of 0.7 K [7] with Cooper pairing. The occurrence of high electron-phonon coupling in another metallic oxide, also a perovskite, became evident with the discovery of superconductivity in the mixed-valent compound $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ by Sleight et al., also a decade ago [8]. The highest T_c in homogeneous oxygen-deficient mixed crystals is 13 K with a comparatively low concentration of carries $n = 2-4 \times 10^{21} \text{ cm}^{-3}$ [9]. Flat electronic bands and a strong breathing mode with a phonon feature near 100 cm^{-1} , whose intensity is proportional to T_c , exist [10]. This last example indicates that within the BCS mechanism, one may find still higher T_c 's in perovskite-type or related metallic oxides, if the electron-phonon interactions and the carrier densities at the Fermi level can be enhanced further.

Strong electron-phonon interactions in oxides can occur owing to polaron formation as well as in mixed-valent systems. A superconductivity (metallic) to bipolaronic (insulator) transition phase diagram was proposed theoretically by Chakraverty [11]. A mechanism for polaron formation is the Jahn-Teller effect, as studied by Höck et al. [12]. Isolated Fe^{4+} , Ni^{3+} and Cu^{2+} in octahedral oxygen environment

show strong Jahn-Teller (J.T.) effects [13]. While SrFe(VI)O_3 is distorted perovskite insulator, LaNi(III)O_3 is a J.T. undistorted metal in which the transfer energy b_e of the J.T. e_g electrons is sufficiently large [14] to quench the J.T. distortion. In analogy to Chakraverty's phase diagram, a J.T.-type polaron formation may therefore be expected at the borderline of the metal-insulator transition in mixed perovskites, a subject on which we have recently carried out a series of investigations [15]. Here, we report on the synthesis and electrical measurements of compounds within the Ba-La-Cu-O system. This system exhibits a number of oxygen-deficient phases with mixed-valent copper constituents [16], i.e., with itinerant electronic states between the non-J.T. Cu^{3+} and the J.T. Cu^{2+} ions, and thus was expected to have considerable electron-phonon coupling and metallic conductivity.

II. Experimental

1. Sample Preparation and Characterization

Samples were prepared by a coprecipitation method from aqueous solutions [17] of Ba-, La- and Cu-nitrate (SPECURE JMC) in their appropriate ratios. When added to an aqueous solution of oxalic acid as the precipitant, an intimate mixture of the corresponding oxalates was formed. The decomposition of the precipitate and the solid-state reaction were performed by heating at 900 °C for 5 h. The product was pressed into pellets at 4 kbar, and reheated to 900 °C for sintering.

2. X-Ray Analysis

X-ray powder diffractograms (System D 500 SIE-MENS) revealed three individual crystallographic phases. Within a range of 10° to 80° (2θ), 17 lines could be identified to correspond to a layer-type perovskite-like phase, related to the K_2NiF_4 structure ($a=3.79$ Å and $c=13.21$ Å) [16]. The second phase is most probably a cubic one, whose presence depends on the Ba concentration, as the line intensity decreases for smaller $x(\text{Ba})$. The amount of the third phase (volume fraction > 30% from the x-ray intensities) seems to be independent of the starting composition, and shows thermal stability up to 1,000 °C. For higher temperatures, this phase disappears progressively, giving rise to the formation of an oxygen-deficient perovskite ($\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14}$) as described by Michel and Raveau [16].

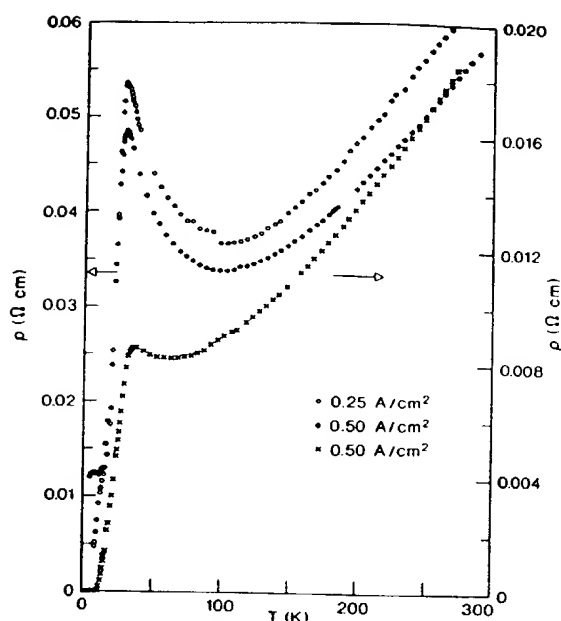


Fig. 1. Temperature dependence of resistivity in $\text{Ba}_x\text{La}_{5-x}\text{Cu}_4\text{O}_{5(3-x)}$ for samples with $x(\text{Ba})=1$ (upper curves, left scale) and $x(\text{Ba})=0.75$ (lower curve, right scale). The first two cases also show the influence of current density

3. Conductivity Measurements

The dc conductivity was measured by the four-point method. Rectangular-shaped samples, cut from the sintered pellets, were provided with gold electrodes and contacted by In wires. Our measurements between 300 and 4.2 K were performed in a continuous-flow cryostat (Leybold-Heraeus) incorporated in a computer-controlled (IBM-PC) fully-automatic system for temperature variation, data acquisition and processing.

For samples with $x(\text{Ba}) \leq 1.0$, the conductivity measurements, involving typical current densities of 0.5 A/cm^2 , generally exhibit a high-temperature metallic behaviour with an increase in resistivity at low temperatures (Fig. 1). At still lower temperatures, a sharp drop in resistivity (> 90%) occurs, which for higher currents becomes partially suppressed (Fig. 1: upper curves, left scale). This characteristic drop has been studied as a function of annealing conditions, i.e., temperature and O_2 partial pressure (Fig. 2). For samples annealed in air, the transition from itinerant to localized behaviour, as indicated by the minimum in resistivity in the 80 K range, is not very pronounced. Annealing in a slightly reducing atmosphere, however, leads to an increase in resistivity and a more pronounced localization effect. At the same time, the onset of the resistivity drop is shifted

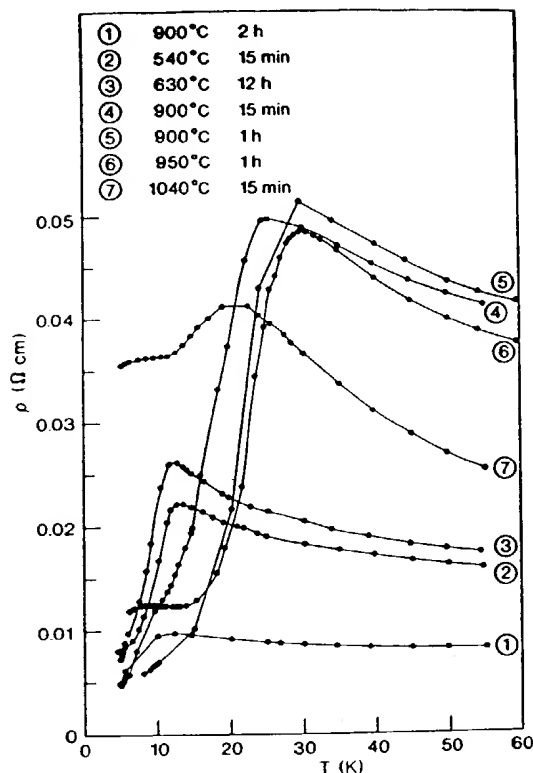


Fig. 2. Low-temperature resistivity of samples with $x(\text{Ba})=1.0$, annealed at O_2 partial pressure of 0.2 bar (curve ①) and 0.2×10^{-4} bar (curves ② to ⑦)

towards the 30 K region. Curves ④ and ⑤, recorded for samples treated at 900 °C, show the occurrence of a shoulder at still lower temperature, more pronounced in curve ⑥. At annealing temperatures of 1,040 °C, the highly conducting phase has almost vanished. As mentioned in the Introduction, the mixed-valent state of copper is of importance for electron-phonon coupling. Therefore, the concentration of electrons was varied by the Ba/La ratio. A typical curve for a sample with a lower Ba concentration of 0.75 is shown in Fig. 1 (right scale). Its resistivity decreases by at least three orders of magnitude, giving evidence for the bulk being superconducting below 13 K with an onset around 35 K, as shown in Fig. 3, on an expanded temperature scale. The latter figure also shows the influence of the current density, typical for granular compounds.

III. Discussion

The resistivity behaviour of our samples, Fig. 1, is qualitatively very similar to the one reported in the Li-Ti-O system, and in superconducting

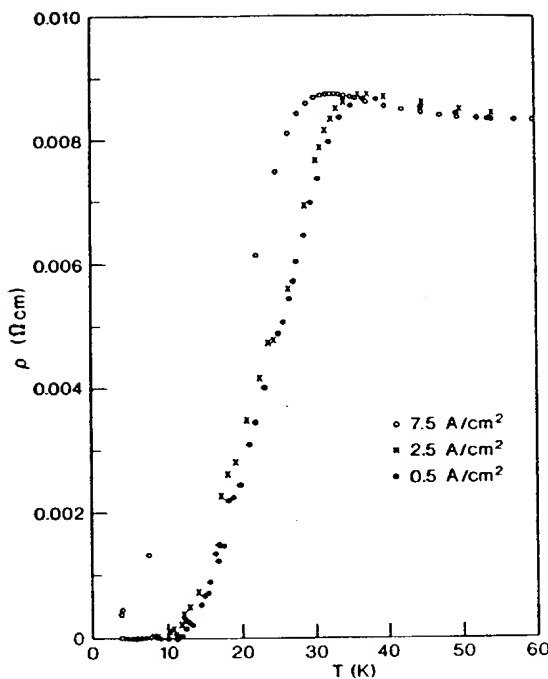


Fig. 3. Low-temperature resistivity of a sample with $x(\text{Ba})=0.75$, recorded for different current densities

$\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ polycrystalline thin films [5, 18]. Upon cooling from room temperature, the latter exhibit a nearly linear metallic decrease of $\rho(T)$, then a logarithmic type of increase, before undergoing the transition to superconductivity. One could, of course, speculate that in our samples a metal-to-metal structural phase transition occurs in one of the phases. The shift in the drop in $\rho(T)$ with increasing current density (Fig. 3), however, would be hard to explain with such an assumption, while it supports our interpretation that we observe the onset of superconductivity of percolative nature, as discussed below. In $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$, the onset of superconductivity has been taken at the resistivity peak [18]. This assumption appears to be valid in percolative systems, i.e., in the thin films [18] consisting of polycrystals with grain boundaries, or when different crystalline phases with interpenetrating grains are present, as found in the Li-Ti-O [5] or in our Ba-La-Cu-O system. The onset can also be due to fluctuations in the superconducting wave functions. We assume one of the Ba-La-Cu-O phases exhibits this behaviour. Therefore, under the above premises, the peak in $\rho(T)$ at 35 K, observed for an $x(\text{Ba})=0.75$ (Fig. 1), has

to be identified as the start to superconductive cooperative phenomena in the isolated grains. It should be noted that in granular Al, Cooper pairs in coupled grains have been shown to exist already at a point where $\rho(T)$ upon cooling has decreased by only 20% of its highest value. This has been proven qualitatively [19] and more recently also quantitatively [20] by the negative frequency shift occurring in a microwave cavity. In 100 Å films, a shoulder in the frequency shift owing to 2D fluctuations was observed above the T_c of the grains. In our Ba-La-Cu-O system, a series of layer-like phases with considerable variety in compositions are known to exist [16, 21], and therefore 2D correlations can be present.

The granularity of our system can be justified from the structural information, and more quantitatively from the normal conductivity behaviour. From the former, we know that more than one phase is present and the question arises how large are the grains. This can be inferred from the logarithmic fingerprint in resistivity. Such logarithmic increases are usually associated with beginning of localization. A most recent example is the Anderson transition in granular Sn films [22]. Common for the granular Sn and our samples is also the resistivity at 300 K, lying in the range of 0.06 to 0.02 Ωcm , which is near the microscopic critical resistivity of $\rho_c = 10 L_0 \hbar / e^2$ for localization. From the latter formula, an interatomic distance L_0 in the range of 100 Å is computed, thus a size of superconducting grains of this order of magnitude must be present. Upon cooling below T_c , Josephson junctions between the grains phase-lock progressively [23] and the bulk resistivity gradually drops to zero by three orders of magnitude, for sample 2 (Fig. 1). At larger current densities, the weaker Josephson junctions switch to normal resistivity, resulting in a temperature shift of the drop, as shown in Fig. 3. The plateau in resistivity occurring below the 80% drop (Fig. 1) for the higher current density of 0.5 A/cm², and Fig. 2 curve (c) may be ascribed to switching of junctions to the normal state.

The way the samples have been prepared seems to be of crucial importance: Michel et al. [21] obtained a single-phase perovskite by mixing the oxides of La and Cu and BaCO₃ in an appropriate ratio and subsequent annealing at 1,000 °C in air. We also applied this annealing condition to one of our samples, obtained by the decomposition of the corresponding oxalates, and found no superconductivity. Thus, the preparation from the oxalates and annealing below 950 °C are necessary to obtain a non-perovskite-type phase with a limited temperature range of stability exhibiting this new behaviour. The formation of this phase at comparatively low temperatures is favoured by the intimate mixture of the compo-

nents and the high reactivity of the oxalates owing to the evolution of large amounts of H₂O and CO₂ during decomposition.

IV. Conclusion

In the concentration range investigated, compounds of the Ba-La-Cu-O system are metallic at high temperatures, and exhibit a tendency towards localization upon cooling. Samples annealed near 900 °C under reducing conditions show features associated with an onset of granular superconductivity near 30 K. The system consists of three phases, one of them having a metallic perovskite-type layer-like structure. The characterization of the new, apparently superconducting, phase is in progress. An identification of that phase may allow growing of single crystals for studying the Meissner effect, and collecting specific-heat data to prove the presence of high T_c bulk superconductivity.

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Note Added in Proof

Chemical analysis of the bulk composition of our samples revealed a deviation from the ideal La/Ba ratios of 4 and 5.66. The actual ratios are 16 and 18, respectively. This is in agreement with an identification of the third phase as CuO.